cur just above E_F. Peaks separated by ~10 eV would be expected from a mixture of neutral and charged molecules.

Further support for the lack of $TCNQ^0$ in TTF-TCNQ is based on the recently reported molecular monopole transition in TCNQ.[12] As momentum transfer is increased in an IES experiment, a sharp peak due to an optically forbidden transition in $TCNQ^0$ appears at 5.3 eV. We repeated the same experiment on TTF-TCNQ and found no such momentum-dependent peak, indicating the absence of $TCNQ^0$ in TTF-TCNQ.

We conclude that while x-ray diffraction experiments may be consistent with less than 100% charge transfer in TTF-TCNQ,[13] IES spectra from bulk samples show no such effects at small (5 eV) and large (400 eV) energy losses.

We are grateful to A. J. Epstein and D. J. Sandman for many fruitful discussions and to W. D. Grobman for constructive and illuminating criticism.

[1]A. J. Berlinsky, J. F. Carolan, and L. Weiler, Solid State Commun. 15, 795 (1974).

[2]J. J. Ritsko, D. J. Sandman, A. J. Epstein, P. C. Gibbons, S. E. Schnatterly, and J. Fields, Phys. Rev. Lett. 34, 1330 (1975).

[3]F. C. Brown and R. Bachrach, private communication.

[4]P. Nielsen, A. J. Epstein, and D. J. Sandman, Solid State Commun. 15, 53 (1974).

[5]J. J. Ritsko, S. E. Schnatterly, and P. C. Gibbons, Phys. Rev. Lett. 32, 671 (1974).

[6]T. J. Kistenmacher, T. E. Phillips, and D. O. Cowan, Acta Crystallogr. B30, 763 (1974).

[7]R. S. Swingle, R. P. Groff, and B. M. Monroe, Phys. Rev. Lett. 35, 452 (1975).

[8]W. D. Grobman, R. A. Pollak, D. E. Eastman, E. T. Maas, Jr., and B. A. Scott, Phys. Rev. Lett. 32, 534 (1974).

[9]N. O. Lipari and C. B. Duke, J. Chem. Phys. 63, 1748, 1768 (1975).

[10]N. O. Lipari, P. Nielsen, J. J. Ritsko, A. J. Epstein, and D. J. Sandman, to be published.

[11]M. A. Butler, J. P. Ferraris, A. N. Bloch, and D. O. Cowan, Chem. Phys. Lett. 24, 600 (1974).

[12]J. J. Ritsko, N. O. Lipari, P. C. Gibbons, S. E. Schnatterly, J. R. Fields, and R. Devaty, Phys. Rev. Lett. 36, 210 (1976).

[13]F. Denoyer, R. Comès, A. F. Garito, and A. J. Heeger, Phys. Rev. Lett. 35, 445 (1975).

Phason Instability in Tetrathiafulvalene-Tetracyanoquinodimethane (TTF-TCNQ)†

Per Bak
Brookhaven National Laboratory, Upton, New York 11973
(Received 24 June 1976)

The 49-K phase transition in tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) is interpreted in terms of a phason instability of the charge-density-wave ground state. The order parameter couples linearly to an external strain, and the phase transition can be suppressed by clamping the crystal. Recent neutron scattering experiments show indications of this effect. Renormalization-group calculations yield pure classical critical behavior at this phase transition, and *XY* exponents for the 54-K transition.

X-ray[1] and neutron-scattering[2] studies of tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) have shown evidence of structural phase transitions with a number of unusual features. At 54 K there is a Peierls-like distortion to an incommensurate structure with modulation wave vector $\vec{q} = (a^*/2, 0.295b^*, 0)$. At 38 K there is a first-order transition to a structure where the modulation vector in the a^* direction has decreased to $a^*/4$. Recently it was predicted that there should in fact be *three* transitions.[3] One set of chains orders at 54 K and the second set of chains orders at 47 K. The modulation wave vector in the a^* direction is $a^*/2$ between 54 and 47 K, and decreases as $a^*/2 - \lambda(47\ \mathrm{K} - T)^{1/2}$ between 47 and 38 K where it locks to a value of $a^*/4$. This behavior has been confirmed by a very recent experiment by Ellenson *et al.*[4] The new transition was found to occur at 49 K rather than 47 K. Knight-shift measurements[5] also indicate a phase transition near 49 K. In this paper, the properties of the 49-K transition will be analyzed from a theoretical point of view. We shall see that this transition is triggered by a soft "phason" mode. The phasons[6] are the elementary excitations of the charge-density-wave (CDW) ground state between 54 and 49 K.

Figure 1 indicates schematically the behavior of the CDW's on one type of chains (TCNQ) at the phase transitions (see Ref. 3). The high-tempera-

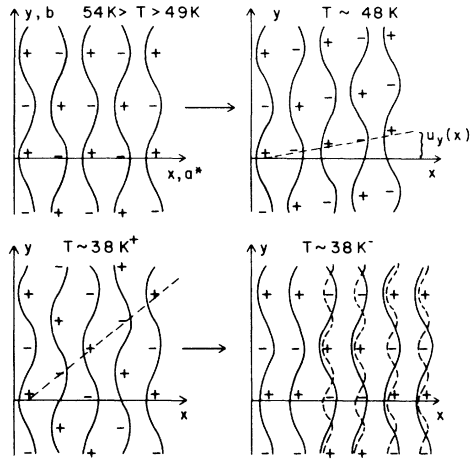

FIG. 1. Schematic diagram of phase transition in TTF-TCNQ. The full curves indicate the q_b modulation along TCNQ chains. The dotted curves indicate the $2q_b(4k_F)$ modulation below 38 K.

ture space group of TTF-TCNQ is $P2_1/c$ and the corresponding point group is C_{2h}.[7] Below 54 K the amplitude of an incommensurate CDW increases with neighboring planes of the same type of molecules in antiphase. The translational symmetry in the b direction is broken, but the point-group symmetry remains the same. At 49 K the CDW's start sliding in the b direction in a uniform way relative to each other. It is this displacement which shows up as a continuous change of the a^* component of the satellites in a neutron-scattering experiment. The distortion of the CDW ground state removes the twofold axis of the point group and changes the overall symmetry from monoclinic to triclinic. As the temperature approaches 38 K, neighbor planes are approximately 90° out of phase. Again the CDW's slide with respect to each other along b, this time discontinuously so that below 38 K the chains are pairwise in phase and neighbor pairs are 180° out of phase. In this picture of the 38-K transition, which differs slightly from that presented in Ref. 3, the lock-in state below 38 K is a superposition of CDW's with wave vectors $\vec{q}_\pm = (\pm a^*/4, 2k_F, 0)$ and with amplitudes $\Phi_{\vec{q}_\pm}$. Clearly, second harmonics with wave vectors $\vec{q}' = (0, 4k_F, 0)$ are generated because of terms like $\Phi_{\vec{q}_+}\Phi_{\vec{q}_-}\Phi_{\vec{q}'}$ in an expansion of the free energy. This is in agreement with a recent x-ray experiment by Kagoshima, Anzai, and Ishigura[8] who observed scattering corresponding to wave vector $\vec{q}'$. However, one can show that the lock-in state on the other type of chain will have a $q = 2q_+ = (a^*/2, 4k_F, 0)$ component,[9] so that scattering with this wave vector should also be observable below 38 K. At 38 K the full monoclinic point symmetry is restored.

To understand the 49-K transition let us consider the incommensurate CDW state between 54 and 49 K. Near 54 K the CDW will contain only one b^* component with amplitude $\Phi_{q_a,q_b} = \Phi_{1/2,q_b} = \Phi_{q_b}$, but as the temperature is lowered other components will in general be induced because of terms like

$$a\Phi_{q_b}\Phi_{q_{b1}}\cdots\Phi_{q_{bn}}\delta(q_b + q_{b1} + \ldots + q_{bn} - K) \qquad (1)$$

in an expansion of the free energy. K is a reciprocal lattice vector in the b^* direction. If one neglects all umklapp terms (with $K \neq 0$), it is easily seen that the free energy remains *unchanged* with respect to a uniform shift, u_y, in the b direction of the CDW state including all different q_b components, with respect to the underlying lattice. [The umklapp terms change by a phase $\exp(iKu_y)$ and act like periodic potentials for the CDW displacement.] The Goldstone mode corresponding to this continuous symmetry is the phason mode introduced by Overhauser.[6] The $\vec{k} = 0$ phason describes a uniform shift, $u_y(\vec{r}) = u_0$, of the CDW ground state in the b direction, and the finite-$\vec{k}$ phasons are quantized phase modulations of the CDW state, $u_y(\vec{r}) = u_{\vec{k}} \exp(i\vec{k}\cdot\vec{r})$. The phason mode is a hydrodynamic mode since $E(k = 0) = 0$. The increase of potential energy caused by a phason fluctuation may be expanded around $k = 0$:

$$E(k) = e_0 k_x^2 + f_0 k_y^2 + g_0 k_z^2, \qquad (2)$$

where we have chosen a coordinate system with the x, y, and z axes along a^*, b, and c, respectively, and $e_0, f_0, g_0 > 0$. The dispersion relation for the phason mode is

$$\rho'\omega^2 = e_0 k_x^2 + f_0 k_y^2 + g_0 k_z^2, \qquad (3)$$

where ρ' is an effective mass density of the phasons. If at a temperature T_2' one of the coefficients, say e_0, is zero, then the $k_x \to 0$ phason goes soft (the phason velocity goes to zero), and, according to (2), the CDW state becomes unstable with respect to long-wavelength phason fluctuations. *The soft phason will condense into a uniform distortion of the CDW in a way perfectly similar to the homogeneous structural phase transition triggered by an acoustic phonon instability.* Whereas the order parameter describing a $k = 0$ structural phase transition is a uniform strain of the lattice, $\epsilon_6 = du_y^L(\vec{r})/dx$, the order parameter describing this new type of phase tran-

sition is a uniform strain of the CDW, $\epsilon_6' = du_y(\vec{r})/dx$. The phasons are the fluctuations of the order parameter. This is exactly what happens at the 49-K transition in TTF-TCNQ (see Fig. 1). The natural order parameter, ϵ_6', of this phase transition is related to the order parameter $q = (q_a - \frac{1}{2})$ of Ref. 3 by the relation $\epsilon_6' = q/q_b$. Hence, although in a neutron scattering experiment all the satellites occur at *finite* wave vectors, the order parameter belongs strictly to a $k = 0$ representation of the space group and transforms like the B representation of the point group. This property gives rise to several experimentally observable effects.

An interesting feature is that ϵ_6' transforms according to the same representation as the ϵ_4 and ϵ_6 strains. The order parameter therefore interacts *linearly* with these strains. Again, one may wonder how such an interaction can take place since the CDW state is composed of finite wave-vector components and the strains are $k = 0$ modes, so that momentum conservation seems impossible. However, even if the $q_x \to 0$ acoustic transverse phonons, $u_{q=q_x}{}^L$, do not interact linearly with the CDW, there exist higher-order coupling terms of the form

$$(\Phi_{1/2,-q_b}\Phi_{1/2-q,q_b} - \Phi_{1/2,+q_b}\Phi_{1/2-q,-q_b})u_q{}^L + \text{c.c.}$$
$$= \Phi_0(\Phi_{1/2-q,q_b} - \Phi_{1/2-q,-q_b})u_q{}^L + \text{c.c.}$$

Here $\Phi_0 = \Phi_{1/2,-q_b} = \Phi_{1/2,q_b}$ is the CDW amplitude above 49 K, and $\Phi_{1/2\mp q,q_b}$ represent the phason deviations from the CDW state (see Ref. 6). These terms are linear in the phason fluctuations, but the coupling is a function of the CDW amplitude.

The free energy may be expanded in the order parameters ϵ_6' and the strain. For simplicity it will be assumed that ϵ_6' couples to ϵ_6 only:

$$F = \tfrac{1}{2}e_0\epsilon_6'^2 + D\epsilon_6\epsilon_6' + \tfrac{1}{2}C_{66}\epsilon_6{}^2. \tag{4}$$

C_{66} is the relevant elastic constant. $\frac{1}{2}e_0$ may be written as $a(T - T_2')$, where T_2' is the "clamped" transition temperature. Minimizing with respect to ϵ_6 we get

$$\epsilon_6 = -D\epsilon_6'/C_{66},$$
$$F = (\tfrac{1}{2}\epsilon_0 - D^2/2C_{66})\epsilon_6'^2 = a(T - T_2)\epsilon_6'^2, \tag{5}$$

where $aT_2 = aT_2' + D^2/2C_{66}$. The transition temperature has increased from T_2' to T_2. Simultaneously, a spontaneous lattice distortion given by ϵ_6 develops. This strain lowers the *lattice* symmetry from monoclinic to triclinic. *The 49-K transition can, in fact, be interpreted as a homogeneous structural phase transition triggered by a phason instability.* This transition should be accompanied by a reduction of the effective elastic constant and an increase of the transverse ultrasound attenuation along certain directions in the ac plane. *By simply clamping the crystal ($C_{66} \to \infty$) one may reduce the transition temperature from T_2 to T_2' and in this way suppress the $2k_F$ ordering of the TTF chains.* All experiments which are sensitive to the ordering of the TTF chains, such as susceptibility and NMR measurements, should be affected. The clamping is easily done. The TTF-TCNQ crystals are usually very flat with large ab faces. One should simply fix these planes to a rigid support. In fact, such experiments have inadvertently been done! The neutron scattering experiments by Ellenson *et al.*[4] were performed on two different crystals. One sample (N6) was mounted strain-free whereas the other sample (E9) was physically glued to an aluminum plate. The elastic scans on N6 showed two sharp peaks located at $q_a = \frac{1}{2} \pm q$ below 49 K and one single peak at $q_a = \frac{1}{2}$ above 49 K. In contrast to these two sharp satellite peaks, a broad flat-topped maximum centered around $q_a = \frac{1}{2}$ was observed on E9 in the temperature range 45–49 K. The present analysis suggests that this intensity arises from parts of the crystal which have not yet ordered or have not reached the full equilibrium value of the order parameter because of the nonuniform strain in the crystal (remember, $\epsilon_6 \sim \epsilon_6' \sim q_a - \frac{1}{2}$). Clearly, experiments should be performed on more effectively clamped crystals.

To determine the critical behavior around T_2 we must take into account the fluctuations of the order parameter. From (2) and (3) we note that the phason velocity goes to zero in one particular direction only, and the corresponding Ginsburg-Landau-Wilson Hamiltonian is *singular* around $q = 0$. To second order in $\epsilon_6'(q)$, the Hamiltonian is

$$\mathcal{H} = \frac{1}{2}\sum_{\vec{q}}\left(e_0\frac{q_x^2}{q^2} + f_0\frac{q_y^2}{q^2} + g_0\frac{q_z^2}{q^2} + Aq^2\right)\epsilon_6'(\vec{q})\epsilon_6'(-\vec{q}). \tag{6}$$

The fluctuations are therefore of type I, according to the notation of Cowley.[10] A renormalization-group calculation including the phason fluctuations gives pure classical exponents! One-dimensional effects and critical fluctuations are therefore completely irrelevant at this transition.

for the "quasi one-dimensional system" TTF-TCNQ. The borderline between classical and nonclassical behavior, which is at $d = 4$ for short-range systems, is at $d = 2$ for this system. This explains the perfectly linear behavior of $q_a - \frac{1}{2}$ versus $T_2 - T$ even close to T_2. The phase transition at $T_1 = 54$ K is of a completely different nature. The order parameter belongs to a wave vector $\vec{Q} = (a^*/2, q_b, 0)$, and the star of $\vec{Q}$ consists of the *two* vectors $\pm\vec{Q}$.[3] The order parameter transforms as a *one*-dimensional representation of the group of $\vec{Q}$ (which includes the twofold axis only). The dimensionality of the order parameters is therefore *two* and one should expect three-dimensional xy exponents ($\beta \sim 0.33$, etc.). A rough comparison with experiment[2] indicates that β is indeed *less* than $\frac{1}{2}$, but the data are too sparse to determine β.

Because of the coupling to the acoustic phonons, the elementary excitations of the CDW state are not pure phasons, but are mixed phason-phonon modes. The dispersion relations of the coupled modes may be found from the roots of the determinant of the inverse response matrix (q is in the a^* direction)

$$G^{-1}(q,\omega) = \begin{pmatrix} e_0 q^2 - \rho'\omega^2 & Dq^2 \\ Dq^2 & C_{66} q^2 - \rho\omega^2 \end{pmatrix}. \qquad (7)$$

The diagonal terms are the inverse propagators for the pure modes, and the off-diagonal elements give the interaction. When $T = T_2$ ($\frac{1}{2}\epsilon_0 - D^2/2C_{66} = 0$), there exists a soft coupled-mode solution with $\omega/q \to 0$, as should be expected. The phason modes, or the mixed modes, should be observable using neutron scattering techniques.[6] In the case of $q = 0$ couplings (umklapp terms, impurities, etc., which pin the CDW to the lattice) the distortion of the CDW state at 49 K will not be completely uniform, since the CDW would gain energy by remaining near the potential minimum. A solitonlike description, like the one presented in Ref. 3, where the potential was assumed sinusoidal, should be applied in this case, but the qualitative picture remains the same. However, there will be an energy gap in the phason spectrum due to $q = 0$ oscillations of the CDW in the umklapp potential, which will complicate the dynamic properties of the transition.

I have benefitted from many illuminating discussions with J. D. Axe, R. A. Cowley, V. J. Emery, J. Lynn, A. F. Garito, W. D. Ellenson, S. M. Shapiro, and G. Shirane.

---

†Work supported by the U. S. Energy Research and Development Administration.

[1]F. Denoyer, R. Comès, A. F. Garito, and A. J. Heeger, Phys. Rev. Lett. 35, 445 (1975); S. Kagoshima, H. Anzai, K. Kajimura, and T. Ishiguro, J. Phys. Soc. Jpn. 39, 1143 (1975).

[2]R. Comès, S. M. Shapiro, G. Shirane, A. F. Garito, and A. J. Heeger, Phys. Rev. Lett. 35, 1518 (1975); R. Comès, G. Shirane, S. M. Shapiro, A. F. Garito, and A. J. Heeger, Phys. Rev. B 14, 2376 (1976).

[3]P. Bak and V. J. Emery, Phys. Rev. Lett. 36, 987 (1976).

[4]W. D. Ellenson, R. Comès, S. M. Shapiro, G. Shirane, A. F. Garito, and A. J. Heeger, to be published.

[5]E. F. Rybaczewski, L. S. Smith, A. F. Garito, A. J. Heeger, and B. G. Silbernagel, to be published.

[6]A. W. Overhauser, Phys. Rev. B 3, 3173 (1971); see also W. L. McMillan, Phys. Rev. B 12, 1187 (1975).

[7]T. J. Kistenmacher, T. E. Phillips, and D. O. Cowan, Acta Crystallogr. B30, 763 (1975).

[8]S. Kagoshima, H. Anzai, and T. Ishigura, to be published.

[9]A detailed theory of all the phase transitions, and the 38-K transition in particular, will be presented in a separate publication by the author and V. J. Emery. See also A. Bjelis and S. Barisic, to be published.

[10]R. A. Cowley, Phys. Rev. B 13, 4877 (1976); A. Aharony, Phys. Rev. B 8, 3363 (1973).